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EVALUATION OF GAS PHASE TITRATION TECHNIQUE AS USED FOR CALIBRATION OF NITROGEN DIOXIDE CHEMILUMINESCENCE ANALYZERS

E. Carol Ellis, et al

National Environmental Research Center
Research Triangle Park, North Carolina

April 1975

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A detailed method write-up describing the chemiluminescence procedure for the continuous measurement of nitrogen dioxide (NO_2) in ambient air was developed. Atmospheric concentrations of NO_2 are measured indirectly by the chemiluminescence reaction of nitric oxide (NO) with ozone (O_3). The NO_2 is first thermally reduced to NO before it is reacted with O_3.

The reliability of measurements made by a continuous or instrumental sampling method is strongly affected by its calibration. In the chemiluminescence procedure, an NO_2 analyzer is calibrated by the gas phase titration of NO with O_3 that produces NO_2 stoichiometrically. Significant errors can be introduced into the analyzer calibration if the standard NO cylinder is incorrectly assayed for NO as well as trace NO_2 or if the converter efficiency of the analyzer is always assumed to be equal to 1.0. Provisions are included in the method to eliminate such errors.

The gas phase titration calibration procedure was subjected to a ruggedness test. The results indicate that normal variations in such factors as reaction and mixing chamber volumes, ratio of dilution air flow to flow through the ozone generator, use of difference ozone generators with different dilution air flows, and use of different standard NO levels had little effect on the gas phase titration procedure.

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by

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ABSTRACT

A detailed method write-up describing the chemiluminescence procedure for the continuous measurement of nitrogen dioxide (NO_2) in ambient air was developed. Atmospheric concentrations of NO_2 are measured indirectly by the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). The NO_2 is first thermally reduced to NO before it is reacted with O_3.

The reliability of measurements made by a continuous or instrumental sampling method is strongly affected by its calibration. In the chemiluminescence procedure, an NO_2 analyzer is calibrated by the gas phase titration of NO with O_3 that produces NO_2 stoichiometrically. Significant errors can be introduced into the analyzer calibration if the standard NO cylinder is incorrectly assayed for NO as well as trace NO_2 or if the converter efficiency of the analyzer is always assumed to be equal to 1.0. Provisions are included in the method to eliminate such errors.

The gas phase titration calibration procedure was subjected to a ruggedness test. The results indicate that normal variations in such factors as reaction and mixing chamber volumes, ratio of dilution air flow to flow through the ozone generator, use of different ozone generators with different dilution air flows and use of different standard NO levels had little effect on the gas phase titration procedure.

CONCLUSIONS

The results of a ruggedness test have shown that the gas phase titration procedure for calibrating NO_2 chemiluminescence analyzers is insensitive to normal variations in operating parameters. Close agreement between NO_2 analyzer responses to the same NO_2 concentrations generated by both gas phase titrations and gravimetrically calibrated permeation devices indicates that gas phase titration is also an accurate calibration procedure.

EVALUATION OF GAS PHASE TITRATION TECHNIQUE AS USED FOR CALIBRATION OF NITROGEN DIOXIDE CHEMILUMINESCENCE ANALYZERS

I. INTRODUCTION

It is the responsibility of the Methods Standardization and Performance Evaluation Branch (MSPEB) of the Quality Assurance and Environmental Monitoring Laboratory (QAEML) to standardize and to evaluate various methods for measuring air pollutants to determine their utility. The standardization process usually includes: (1) a review of the procedure write-up to insure that it is clearly written and technically accurate, (2) a laboratory evaluation to determine if the procedure will perform according to the write-up specifications and also if it is flexible enough to withstand minor changes in sampling parameters, i.e., ruggedness testing[1] and (3) a collaborative test to determine the method's precision and accuracy. The MSPEB's evaluation (items 1 and 2 above) of the continuous chemiluminescence procedure[2] for NO_2 is the subject of this report. The report details the results of a procedure review and a laboratory evaluation of the calibration procedure, including a ruggedness test. A collaborative test of the NO_2 chemiluminescence

procedure has been performed under contract to MSPEB, and these results will be reported elsewhere.

The evaluation of a continuous or instrumental sampling method is different from that of a manual method. For example, the chemiluminescence procedure for NO_2 does not and should not specify the analyzer design or its operating parameters. It specifies only that the analyzer operate on the chemiluminescence principle for detection of NO_2 (as NO) and that it meet certain performance specifications. The only section of the method not inherent to the analyzer and its operation is the calibration procedure. This evaluation of the chemiluminescence procedure is in essence an evaluation of the calibration procedure only because it would not be meaningful to evaluate how well one particular analyzer makes use of the detection principle without doing the same for other NO_2 chemiluminescence analyzers.

II. EXPERIMENTATION

A copy of "The Tentative Method for the Continuous Measurement of Nitrogen Dioxide in the Atmosphere (Chemiluminescence Procedure)" is included in Appendix A for easy reference. The reagents and apparatus used in the laboratory evaluation of the gas phase titration calibration technique are described therein.

A. APPARATUS

1. NO_2 Chemiluminescence Analyzer

A Bendix Model 8101-B Oxides of Nitrogen Analyzer that employs the chemiluminescent principle for NO_2 detection was used in the laboratory evaluation. This analyzer meets the performance specifications described in the method.

2. Ozone Analyzer

A Dasibi Model 1003 Ozone Monitor, calibrated by the neutral buffered KI procedure,[3] was used to monitor unreacted ozone during gas phase titrations.

3. Gas Phase Titration Assembly

The assembly is described fully in Section 6.2 of Appendix A.

B. TEST ATMOSPHERE GENERATION

Test atmospheres containing known concentrations of NO_2, NO, and O_3 were necessary for the laboratory study. The details for generation of a standard atmosphere for each gas are outlined below. In each case the dilution gas was compressed house air. It was purified by passage through air filters for particle removal; treatment with O_3

for conversion of NO to NO_2; silica gel for drying; and finally a mixture of activated charcoal (6-14), molecular sieve (6-16 mesh, type 4A), and silica gel (6-16 mesh) for removal of any NO_2, hydrocarbons, or ozone.

1. Nitrogen Dioxide

Test atmospheres containing known concentrations of NO_2 were produced by the gas phase reaction of NO with O_3. Such test atmospheres were used to calibrate the NO_2 response of the chemiluminescence analyzer and to evaluate the calibration procedure. The analyzer calibration was checked with known NO_2 concentrations generated from gravimetrically calibrated NO_2 permeation devices.[4-8]

2. Ozone

Two ozone generators,[9,10] both of identical design and construction, were used to generate known ozone concentrations for gas phase titration. Each generator consists of a quartz tube into which ozone-free air is introduced and then irradiated with a stable low-pressure mercury lamp. The level of irradiation is controlled by an adjustable aluminum sleeve which fits around the lamp; ozone concentrations are varied by adjustment of this sleeve. At a fixed level of irradiation and air flow, ozone is produced at a constant rate.

Ozone generator #14 generates ozone in the range 0-1.0 ppm at a dilution air flow of 2.91 ℓ/min. Generator #8 produces the same range of ozone concentrations at a dilution flow of 5.02 ℓ/min. Both generators were calibrated by the neutral buffered potassium iodide (KI) procedure.[3]

3. Nitric Oxide

Two cylinders of nitric oxide in nitrogen were used to generate known concentrations of NO by flow dilution. Both cylinders were assayed, as described in the method, by gas phase titration with O_3 from the calibrated ozone generators discussed above. Cylinder A contains 114 ppm NO and cylinder B contains 43.0 ppm NO. The cylinders were also analyzed for NO_2 impurity using the TGS procedure[11]; cylinders A and B contain 1.4 and 3.0 ppm NO_2, respectively.

C. FLOW MEASUREMENT

Dilution flow measurements were made with a 1 ℓ/rev wet test meter. The NO flow was measured with a 10 cm^3 soap bubble flow meter. A 100 cm^3 soap bubble flow meter was used to measure the air flow through the ozone generators and also to measure the sample flow of the NO_2 chemiluminescence analyzer. All flow measurements were made at the beginning of each experiment, then again at the end. No flows varied more than 2 percent from the beginning to the end of any experiment.

III. RESULTS AND DISCUSSION

A. PROCEDURE REVIEW

Improvements were made on the "Tentative Method for the Continuous Measurement of Nitrogen Dioxide (Chemiluminescent)" published in the Federal Register.[2] The method write-up was generalized in its discussion of the chemiluminescent principle and in its directions for analyzer adjustments during calibration so that the method would be more applicable to any chemiluminescent NO_2 analyzer. Additions were made to the calibration procedure to minimize the sources of experimental error. A brief discussion of the calibration procedure seems appropriate at this point.

The calibration technique is based upon application of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2.[12,13]

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad k = 1.0 \times 10^7 \text{ liter mole}^{-1} \text{ sec}^{-1} \qquad (1)$$

The quantitative nature of the reaction is used in a manner such that, once the concentration of one component is specified, the concentrations of the other two are determined. In this application the NO is always kept in slight excess to the O_3 concentration.

An assayed NO in N_2 cylinder (50 - 100 ppm) is used to generate known concentrations of NO as well as NO_2 for the respective calibrations of the NO and NO_2 detector responses of a chemiluminescence analyzer. First the NO response is calibrated directly by an

appropriate dilution of the NO gas from the assayed cylinder. Then, to calibrate the NO_2 response of the analyzer, O_3 is added in increments to excess NO. The incremental decrease in NO concentration (observed by noting the NO detector response of the analyzer) is equivalent to the NO_2 produced in the titration. The continuous production of NO_2 in the titration provides a dynamic calibration.

One possible source of error in the calibration procedure is the NO cylinder analysis. It is necessary to analyze the cylinder for both NO and NO_2 because the nominal NO concentration of some cylinders has been found to be inaccurate, and some cylinders have been found to contain as much as 5-10 percent of the nominal NO as NO_2. The NO content of the cylinder is assayed by gas phase titration with O_3. Mixtures containing known O_3 concentration are produced by an ozone generator that has been calibrated by iodometry (neutral buffered KI procedure).[3] The amount of O_3 added in this titration is equivalent to the amount of NO consumed; thus the NO content of the cylinder is determined. Once the cylinder is assayed, it can be used reliably for up to 6 months (EPA laboratory findings) to prepare known concentrations of NO. Since there is always the possibility that NO_2 may be present in trace amounts in the NO cylinder, it is necessary to analyze the NO cylinder for any NO_2 impurity. The concentration of NO_2 in the cylinder must be determined by an independent method which has no appreciable interference from NO; the triethanolamine-guaiacol-sulfite (TGS) manual method[11] is one such method.

Another possible source of error in the calibration procedure is the tacit assumption that the NO_2 converter efficiency of the

chemiluminescence analyzer is always constant and equal to 1.0, i. e., one mole of NO_2 gas is thermally converted to one mole of NO gas in the analyzer's converter prior to detection. This assumption is not always valid; therefore, the NO_2 converter efficiency must be determined prior to analyzer calibration. A scheme for determining the NO_2 converter efficiency is included in the calibration procedure. The efficiency of the NO_2 converter should be constant over the range of operation, and for acceptable analyzer sensitivity the converter should be replaced or rejuvenated should its efficiency drop below 0.9 (90 percent).

B. PRELIMINARY LABORATORY EVALUATION

The Bendix chemiluminescent NO_2 analyzer was calibrated as described in the procedure (Appendix A) by gas phase titration of NO with O_3. The NO was generated from cylinder A (114 ppm NO + 1.4 ppm NO_2), and the O_3 source was generator #14. No ozone was detected by the Disabi ozone monitor throughout the titration. The analyzer NO_2 calibration was verified by checking the analyzer response against an NO_2 standard generated from gravimetrically calibrated NO_2 permeation tubes. A comparison of the analyzer's response to NO_2 generated by gas phase titration and by permeation tubes is shown in Figure 1. The two curves are indistinguishable. The least squares linear regressions for the two curves are

$$A: \quad y = 0.9998\ x - 0.0004$$

$$B: \quad y = 0.9871\ x + 0.0018\ .$$

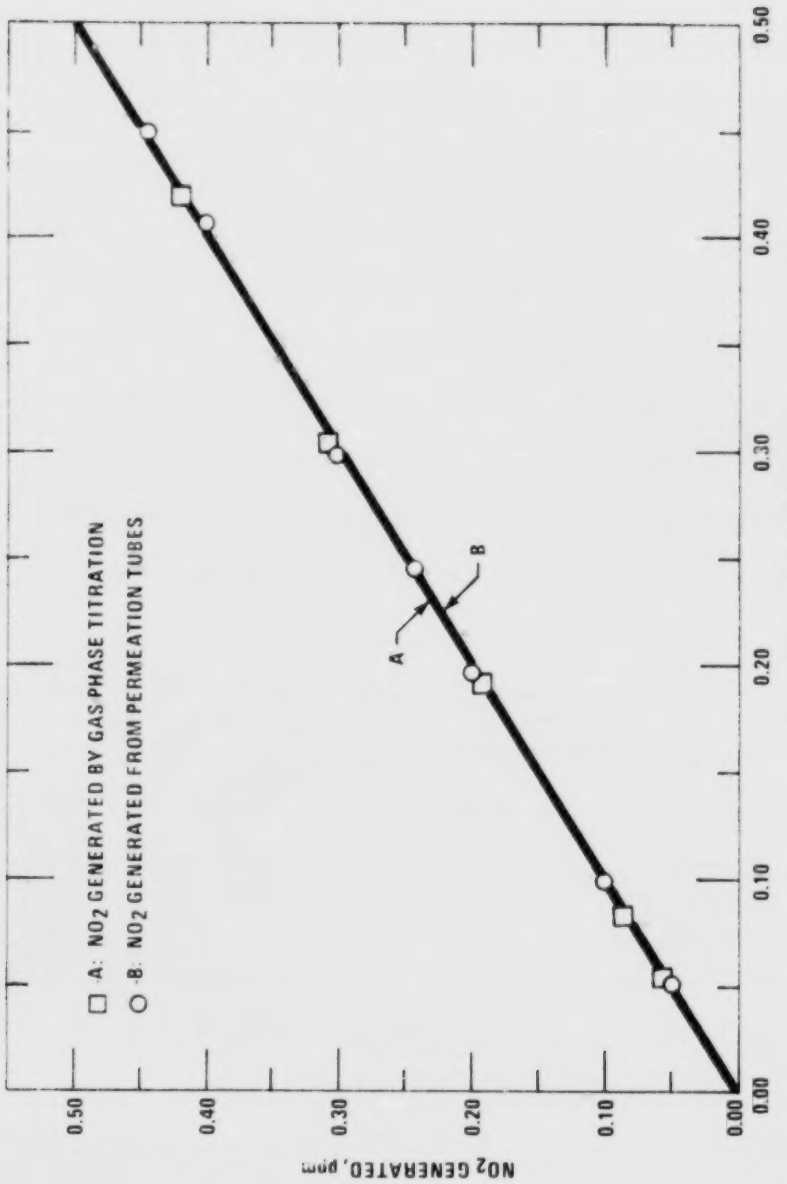

Figure 1. Comparison of NO_2 generated by gas phase titration and by permeation tubes to a chemiluminescence analyzer's NO_2 response.

The gas phase titration was repeated, and this calibration was identical to the first. Since there were no obvious problems involved in the calibration of the one NO_2 analyzer by the gas phase titration procedure, no single variable evaluations seemed necessary and the ruggedness test was initiated.

C. RUGGEDNESS TEST

1. Theory

How is a method or procedure affected by slight changes in operational parameters that might be expected to occur in normal usage? To answer this question, Youden[1] has described a scheme called a ruggedness test for determining the individual effects of variations in several parameters with a minimum number of experiments. In a ruggedness test a series of experiments are conducted in which selected parameters are studied at two levels: the nominal level stated in the method write-up and a challenging level. The effect of a particular variable is determined by comparing the test results obtained at the two levels. Therefore, the parameters which significantly affect the method's response, once identified, can be more stringently controlled.

In Youden's scheme seven[(a)] parameters are chosen for testing, and their nominal values are denoted with the letters A to G. A challenging level for each parameter is then selected and denoted by the corresponding lower case letters, a to g. A series of eight

---

(a) Schemes for examining the effect of a larger or smaller number of variables are available.[14,15]

experiments are then conducted using various combinations of either nominal or challenging values for each variable. The format for these experiments is shown in Table 1.

Each of the eight experiments produces a result, denoted as s, t, u, v, w, x, y, and z. Examination of the format in Table 1 reveals that by summing the group of experimental results in which a given nominal value is involved, and subtracting from it the sum of the group of results in which the corresponding challenging value is involved, the effect of all other variables is cancelled. If the grouped results are divided by the number in each group, the above subtraction will yield the average effect or difference between the nominal and challenging conditions. For example, the average effect of variable C is calculated as follows:

$$C - c = \frac{s + u + w + y}{4} - \frac{t + v + x + z}{4} .$$

A complete set of equations for calculating the effect of A-a, B-b, etc. are given in Appendix B.

It should be noted that the results of a ruggedness test will not describe completely the effect of varying a given parameter. The results will only show an effect due to the range of variation used in the test. If an effect is shown by the ruggedness test to be significant, further experimentation will be necessary to define the exact relationship between variation of the parameter and the method's response. It should also be noted that the various parameters are assumed to be mutually independent.

Table 1. RUGGEDNESS TEST FORMAT

	Determination number							
Factor value	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Observed result	s	t	u	v	w	x	y	z

2. Design

The ruggedness test described by Youden provides for evaluation of seven variables. When only five or six variables seem important, then dummy variables can be substituted for the remaining variables. The effect from a dummy variable should be small. If the effect of varying a dummy variable should give a large result, some explanation should be sought. In the case of the gas phase titration calibration procedure, five real parameters are tested; the remaining two are labeled as dummies.

a. Dummy (No variation)

b. Reaction Chamber Volume

A kjeldahl connecting bulb with a volume of approximately 250 cm^3 is used for the NO + O_3 reaction chamber. Reduction of reaction chamber volume to 125 cm^3 should cut down on the residence time for the two gases in the chamber and might affect the completeness of the reaction.

c. Mixing Chamber Volume

The mixing chamber is also a 250 cm^3 kjeldahl bulb. A reduction of the mixing chamber volume to 125 cm^3 might have some affect on the homogeneous mixing of the NO and NO_2 (from NO + O_3) calibration mixture with the dilution air.

d. Flow Ratio

The air stream is split upstream of the ozone generator to allow only 1/10 to 1/15 of the total air flow to go through

the ozone generator, with the remainder bypassing the generator to the mixing chamber. The air stream is split in order to permit low flows through the ozone generator to create locally high concentrations of O_3 and NO in the reaction chamber. At these high concentrations and low flows, the reaction chamber provides sufficient residence time for quantitative reaction to occur. The nominal flow ratio of 10:1 is challenged by a ratio of 5:1.

e. Ozone Generator

The calibration procedure specifies the use of an ozone source capable of producing 0 to 1.0 ppm O_3 at a total air flow of 2 to 10 ℓ/min. Ozone generator #14 with a total air flow of 2.91 ℓ/min was used in calibrating the NO_2 chemiluminescence analyzer; therefore, it is designated as the nominal generator. The challenging ozone source is generator #8 with a total air flow of 5.02 ℓ/min.

f. Level of NO in Standard Cylinder

The procedure suggests either a 50 or a 100 ppm NO cylinder for the NO calibration standard. Since the most commonly used NO cylinder concentration is about 100 ppm, the nominal NO standard level was set at about 100 ppm. The approximately 50 ppm cylinder is the challenging level. The NO flow from a 50 ppm cylinder into the reaction chamber would be twice the flow from the 100 ppm cylinder needed to generate comparable NO atmospheres. The higher flow from the 50 ppm cylinder might decrease the residence time of the NO in the reaction chamber and, in turn, affect the completeness of the NO + O_3 reaction.

g. Dummy (No variation)

3. Procedure

The selected parameters were incorporated into the ruggedness test format as shown in Table 2. Experiments were conducted in random order (2, 6, 7, 1, 3, 5, 4, and 8) using the previously calibrated NO_2 chemiluminescence analyzer. Zero and span checks were made prior to each experiment, and the points were always within 1 percent of the original analyzer calibration. In each experiment the NO_2 analyzer response was noted as the NO_2 concentration generated by gas phase titration was varied from 0 to 0.5 ppm in 0.1 ppm increments. The result of each gas phase titration experiment is expressed as the slope of the calibration curve, i.e., NO_2 concentration generated vs. NO_2 analyzer response. All the test results are given in Appendix C.

4. Results

The ruggedness test results listed in Appendix C were substituted into the equations of Appendix B, and the effect of each parameter was calculated. A summary of the ruggedness test results are shown ranked in order of absolute magnitude in Table 3. The largest difference measured is only 2.4 percent. Since the errors involved in reading the chemiluminescence analyzer and in generating standard NO, NO_2, and O_3 atmospheres are at least 2 percent, the differences measured by the ruggedness test are insignificant.

Table 2. RUGGEDNESS TEST FORMAT FOR CALIBRATION OF NO_2 ANALYZERS BY GAS PHASE TITRATION

Factor value	Determination number							
	1	2	3	4	5	6	7	8
Dummy A = a, No variation	---	---	---	---	---	---	---	---
Reaction Chamber Volume B = 250 cm^3 b = 125 cm^3	250 cm^3	250	125	125	250	250	125	125
Mixing Chamber Volume C = 250 cm^3 c = 125 cm^3	250 cm^3	125	250	125	250	125	250	125
Flow Ratio D = 10:1 d = 5:1	10:1	10:1	5:1	5:1	5:1	5:1	10:1	10:1
Ozone Generator & Air Flow E = ~3.0 ℓ/min e = ~5.0 ℓ/min	3.0 ℓ/min	5.0	3.0	5.0	5.0	3.0	5.0	3.0
Level of NO in Standard Cylinder F = ~100 ppm f = ~50 ppm	100 ppm	50	50	100	100	50	50	100
Dummy G = g, No variation	---	---	---	---	---	---	---	---
Observed Result	s	t	u	v	w	x	y	z

Table 3. SUMMARY OF RUGGEDNESS TEST RESULTS

Rank	Factor	Difference, %
1	Reaction Chamber Volume 250 cm^3 vs. 125 cm^3	(-) 2.39
2	Dummy	1.61
3	Flow Ratio 10:1 vs. 5:1	(-) 0.68
4	Mixing Chamber Volume 250 cm^3 vs. 125 cm^3	0.48
5	Level of NO in Standard Cylinder ~100 ppm vs. ~ 50 ppm	0.42
6	Ozone Generator Air Flow ~ 3.0 ℓ/min vs. ~ 5.0 ℓ/min	(-) 0.34
7	Dummy	(-) 0.12

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APPENDIX A. TENTATIVE METHOD FOR CONTINUOUS MEASUREMENT OF NITROGEN DIOXIDE IN ATMOSPHERE (CHEMILUMINESCENCE PROCEDURE)

AUGUST 1974

[a] A tentative method is one that has been carefully drafted from availabel experimental information, reviewed editorially within the Methods Standardization and Performance Evaluation Branch, EPA, and has undergone extensive laboratory evaluation. The method is still under investigation and, therefore, is subject to revision.

1. Principle and Applicability

1.1 Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3) at reduced or near atmospheric pressures.[1-4] NO_2 is first thermally converted[5] (reduced) to NO before it is reacted with O_3. A photomultiplier tube detector measures the intensity of the light from the resulting chemiluminescent reaction. Since ambient air usually contains NO_2 and NO simultaneously, some means must be provided for distinguishing between the NO concentration already in the sample and the NO concentration resulting from the reduction of NO_2 to NO. Ambient air is drawn directly into the detector assembly to determine the NO concentration. The NO_x concentration ($NO + NO_2$) is measured when the air is passed through the thermal converter and then into the detector. The NO_2 concentration is then determined electronically by subtracting the NO detector response (or concentration) from the NO_x detector response. The measurement is accomplished in approximately one minute.

1.2 The procedure is applicable to the continuous measurement of NO_2 in ambient air.

2. Range and Lower Detectable Limit

2.1 Analyzers with full scale ranges from 0 to 376 $\mu g/m^3$ (0 to 0.2 ppm) to 0 to 18,800 $\mu g/m^3$ NO_2 (0 to 10 ppm) are available. For normal ambient air measurements the most sensitive range on the

analyzer should be used, not to exceed a sensitivity of 0 to 940 $\mu g/m^3$ (0 to 0.5 ppm). Separate range selectors should be made available for NO, NO_2, and NO_x since NO_x concentrations sometimes exceed 1 ppm.

2.2 The lower detectable limit is approximately 20 $\mu g/m^3$ (0.01 ppm) at the 0 to 940 $\mu g/m^3$ (0-0.5 ppm) range.

3. Interferences

3.1 The chemiluminescent detection of NO with O_3 is not subject to interference from any of the common air pollutants such as O_3, NO_2, CO, NH_3, and SO_2.[1] The elimination of possible hydrocarbon interference is achieved by means of a red sharp-cut optical filter.

3.2 Any compounds which will be converted to NO in the thermal converter will interfere with the measurement of the NO_x ($NO + NO_2$) concentration. The principal compound of concern is ammonia; however, it is not an interferent at converter temperatures below 300^o C. Unstable nitrogen compounds, such as peroxyacetylnitrate (PAN) and organic nitrites decompose thermally to form NO. However, their ambient concentrations are usually so low that their interference can be disregarded.[6]

4. Apparatus

4.1 Nitrogen Dioxide Analyzer. The analyzer should be of the chemiluminescent type with a linear response over the desired

range. The analyzer should meet or exceed the specifications described in Appendix A-1. See Figure A-1 for a general schematic of a typical chemiluminescence analyzer.

5. Procedure

5.1 Ambient air is drawn into the analyzer with a sample pump or with the vacuum pump used in the detector assembly. Ozonized oxygen or air at a constant flow is drawn into the detector assembly to react with the sample. For exact operating procedures refer to the analyzer instruction manual.

6. Calibration

6.1 Principle. The calibration technique is based upon application of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2.[2,3]

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad k = 1.0 \times 10^7 \text{ liter mole}^{-1} \text{ sec}^{-1} \qquad \text{(A-1)}$$

The quantitative nature of the reaction is used in a manner such that, once the concentration of one component is specified, the concentrations of the other two are determined. The gas phase titration is carried out in the presence of excess NO to prevent formation of higher oxides of nitrogen through further oxidation of NO_2 by O_3.

Atmospheres of known O_3 concentration are produced from an ozone generator, the output of which has been calibrated by

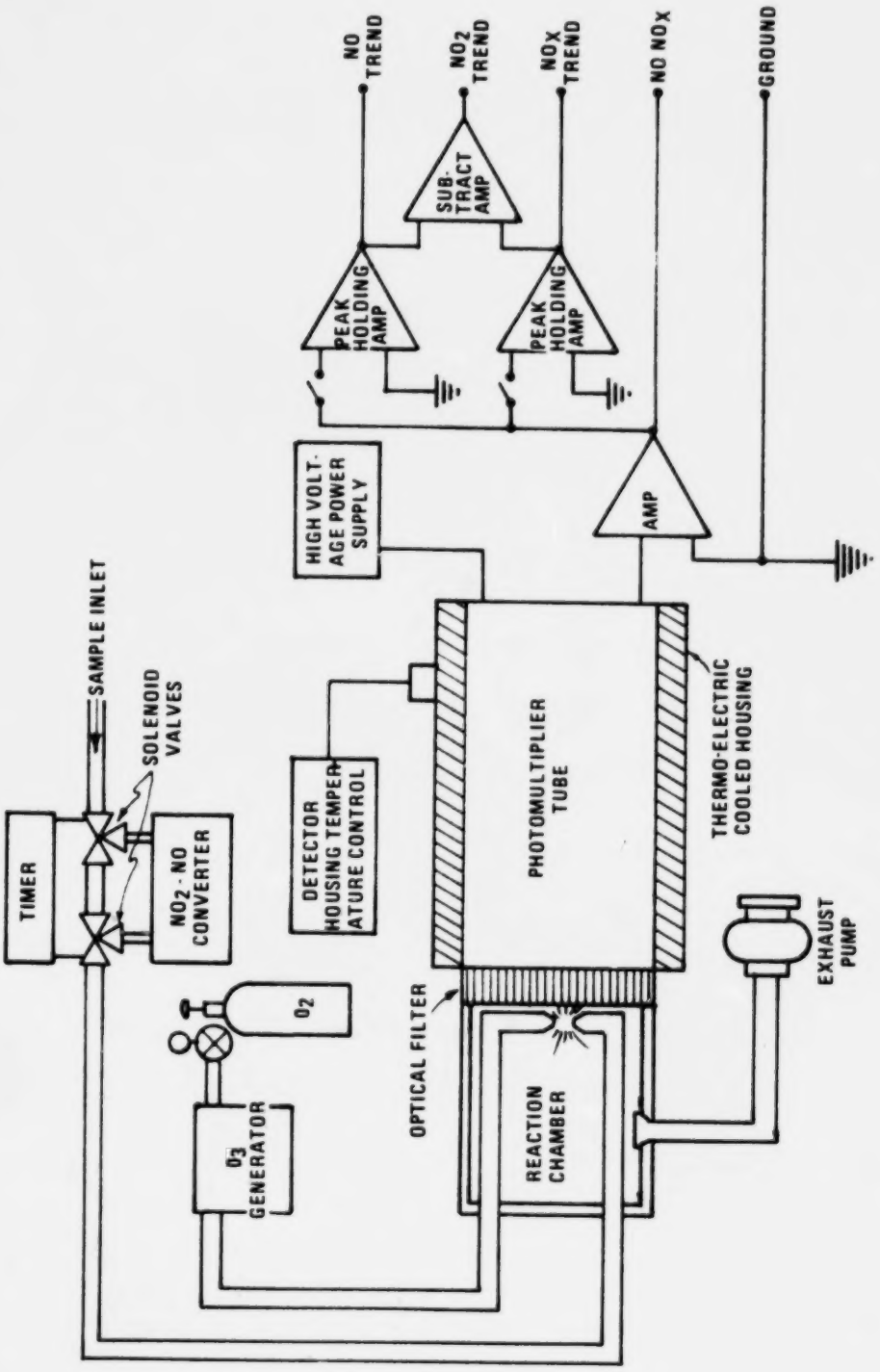

Figure A-1. Automated NO, NO_2, NOX chemiluminescence analyzer.

iodometry (neutral buffered KI procedure).[7] The NO content of an NO in N_2 cylinder (50-100 ppm) is then assayed by gas phase titration with the O_3. Analysis of the NO cylinder is necessary because the nominal NO concentration provided by some manufacturers is sometimes inaccurate. The amount of O_3 added in the titration is equivalent to the amount of NO consumed (or NO_2 produced), thus the NO content of the cylinder can be determined.

Once the cylinder is assayed it can be used to prepare known concentrations of NO. The analysis should be repeated at 6-month intervals. In addition to generating standard NO concentrations for calibration the NO response of an analyzer, the assayed NO cylinder is also used to generate known NO_2 concentrations by a gas phase titration with O_3. To calibrate the NO_2 response of a chemiluminescence analyzer, O_3 is added in increments to excess NO. The incremental decrease in NO concentration (observed by noting the NO detector response of the analyzer) is equivalent to the NO_2 produced in the titration. Since the NO_2 is produced continually in the titration, a dynamic calibration results.

6.2 Apparatus. A schematic drawing of the gas phase titration apparatus is shown in Figure A-2.

6.2.1 Pressure regulator for NO cylinder. A regulator to fit the NO cylinder having internal parts of stainless steel with a Teflon or Kel-F seat and a delivery pressure of 30 psi. Note: This regulator as well as needle valve and delivery lines should be thoroughly flushed <u>after</u> connecting to the NO cylinder. Flushing

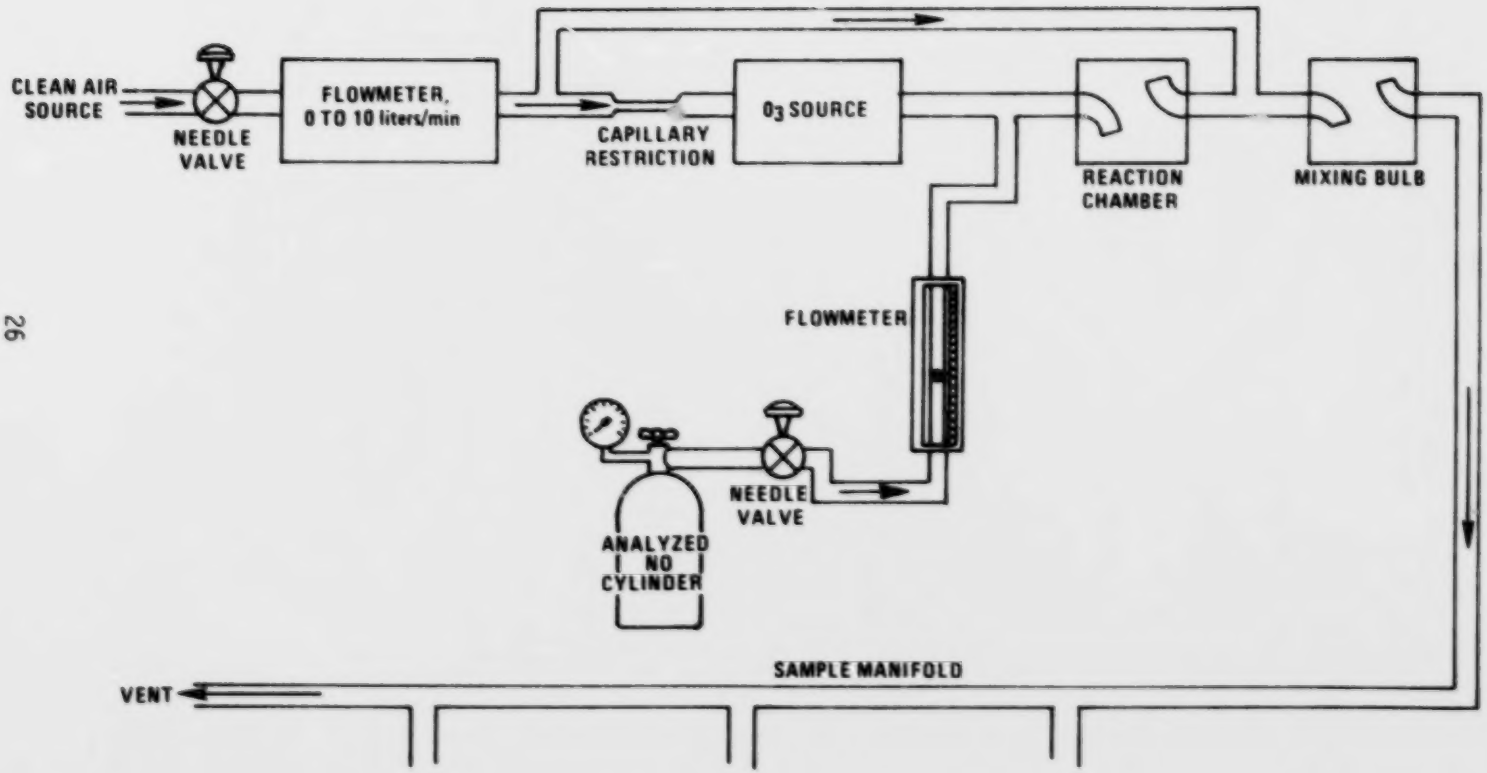

Figure A-2. Flow scheme for calibration of NO, NO_2 and NO_X monitor by gas phase titration.

can be accomplished by adjusting the delivery pressure to near maximum and venting the gas for several minutes.

6.2.2 Needle valves. Stainless steel parts are required in controlling the NO flow. Material of component parts is not critical for control of air flow.

6.2.3 Flowmeters

6.2.3.1 NO flow. A flowmeter capable of monitoring NO flows between 0-100 cm^3/min. A 25 cm^3 capacity soap bubble flowmeter is required for measuring absolute NO flows.

6.2.3.2 Air Flow. A flowmeter capable of monitoring flows between 0 and 10 ℓ/min. A large soap bubble meter or wet test meter is required for calibration of the flow meter and for making absolute flow measurements in this range.

6.2.4 Capillary restrictor. Glass or stainless steel capillary of the proper I.D. and length to maintain a 1:10 to 1:15 ratio of air flow through the generator to total air flow. A Teflon or stainless steel needle valve can be used in place of a capillary restrictor provided that a stable flow through the generator is maintained.

6.2.5 Calibrated Ozone Generator. Capable of producing O_3 over the range 0 to 1 ppm at a total air flow rate of 2 to 10 ℓ/min. One such ozone source consists of a quartz tube into which ozone-free air is introduced and then irradiated with a stable low-pressure mercury lamp.[8,9] The level of irradiation of the quartz tube is controlled by an adjustable aluminum sleeve which fits around the

lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of air flow and irradiation, ozone is produced at a constant rate.

6.2.6 Reaction Chamber and Mixing Bulb. Kjeldahl connecting bulbs with volumes of approximately 250 cm^3 should be used.

6.2.7 Sample Manifold. A multiport all-glass manifold should be used. All connections in the calibration system should be glass or Teflon.

6.3 Reagents

6.3.1 Nitric Oxide. Cylinder containing approximately 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. In ordering cylinders from commercial vendors, specify the use of O_2 free N_2. This will minimize NO_2 formation.

6.3.2 Clean Air Source. Compressed (house) or cylinder air containing no more than 0.005 ppm of NO, NO_2, and O_3, or reactive hydrocarbons. The air is cleaned by passing it through silica gel for drying, treating with ozone to convert any NO to NO_2, and finally by passing through activated charcoal (6-14 mesh), and molecular sieve (6-16 mesh, type 4A), to remove any NO_2, hydrocarbons, and excess O_3. Regardless of the source of air, compressed (house) or cylinder air, it should be purified as described above.

6.4 Procedure. The gas phase titration apparatus shown in Figure 2 is used to assay the NO cylinder and also to generate NO_2 for analyzer calibration. NO from the cylinder is diluted with a constant flow of clean air (with the ozone source set at zero O_3

concentration) to produce an NO concentration at the sample manifold of approximately 1 ppm. The ozone source is then adjusted to produce incremental increases in O_3 concentration which result in equivalent incremental decreases in NO concentration down to approximately 0.05 ppm NO. During this titration NO_2 is generated in amounts equivalent to the NO consumed by the O_3.

Upstream of the ozone generator, the air stream is split such that the capillary restrictor allows only 1/10 to 1/15 of the total air flow to go through the ozone generator, with the remainder bypassing the generator. The air stream is split in order to permit low flows through the ozone generator to create locally high concentrations of O_3 and NO in the reaction chamber. At these high concentrations and low flows, the reaction chamber provides a residence time long enough for quantitative reaction to occur. The NO-NO_2 mixture is combined with the bypassed air in the mixing chamber. The turbulent flow created assures a homogeneous sample at the sample manifold.

6.4.1 Analysis of NO cylinder by Gas Phase Titration (G.P.T.). Allow the chemiluminescence analyzer to sample clean air until a stable response is obtained. After the response has stabilized, make proper zero adjustment. Determine the NO concentration in the cylinder as follows. With the NO flow off, set the clean air flow at approximately 2 to 10 ℓ/min. (the actual flow depends on the operating characteristics of the ozone generator, Section 6.2.5). Measure and record the absolute air flow, F_o. Adjust the NO flow

to generate approximately 0.9 ppm NO at the manifold. (Use the NO cylinder concentration provided by the manufacturer.) Measure and record the absolute NO flow, F_{NO}. Adjust the span control for NO response on a 0 to 1 ppm range so that the NO response reads exactly the NO concentration generated. After the NO response has stabilized, record the reading and then add approximately 0.1 ppm O_3 by adjustment of the calibrated ozone source. (The ozone source should be stable before beginning the gas phase titration.) Allow the NO response to stabilize and record the reading. (Readings may be taken directly from the instrument readout or from a properly spanned recorder.) Adjust the ozone source to obtain approximately 0.2 ppm O_3 and allow the NO response to stabilize. Continue this procedure until up to 0.8 to 0.9 ppm O_3 has been added in a stepwise fashion. A minimum of six ozone additions are required to accurately define the calibration curve. Remeasure F_0 and F_{NO} to determine whether the flows have changed during the titration.

6.4.1.1 Calculation. Plot the O_3 concentration added (y-axis) versus the resultant NO concentration in ppm (x-axis). A linear curve should be obtained. (See Figure A-3, for example.) The O_3 concentration at the y-axis intercept, C'_0, is the O_3 equivalent to the initial diluted NO concentration. The cylinder NO concentration is calculated as follows:

$$C_{NO} = \frac{F_0 \times C'_0}{F_{NO}} \qquad \text{(A-2)}$$

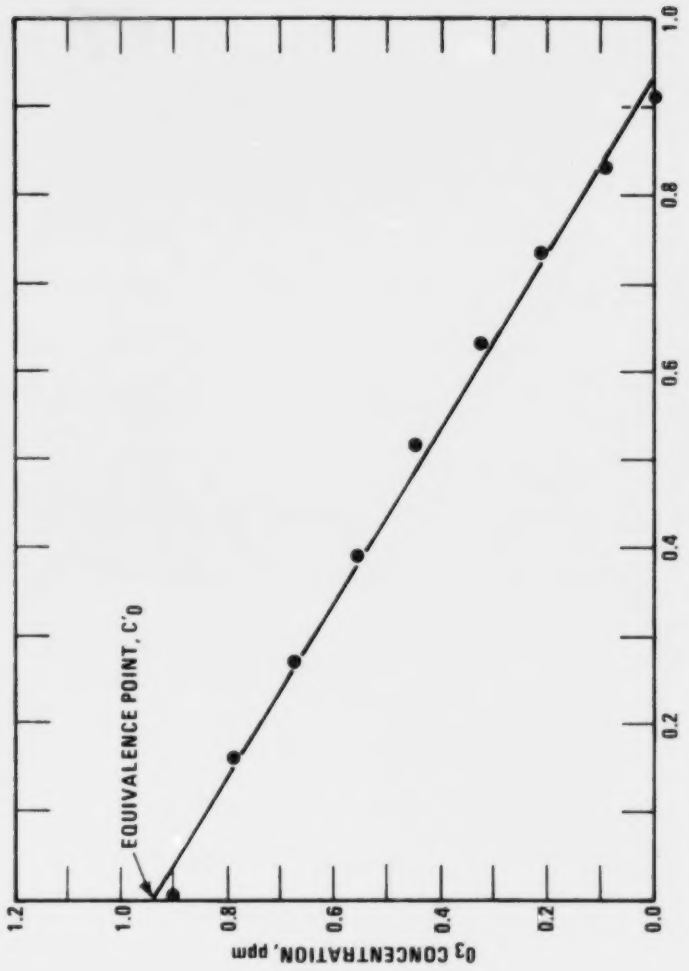

Figure A-3. Gas phase titration of NO with O_3.

where: C_{NO} = cylinder NO concentration, ppm

F_{NO} = measured NO flow, cm^3/min

C'_O = O_3 equivalence point, ppm

F_O = total clean air flow, cm^3/min

6.4.2 NO_2 Impurity in the NO Cylinder. The concentration of NO_2 in the NO cylinder must be determined because the error in disregarding this impurity can be significant. Consider, for example, a 100 ppm NO cylinder with only 1 ppm of NO_2. When used to generate 1 ppm NO for G.P.T., the NO_2 is diluted to 0.01 ppm. Although this is a small amount of NO_2, the error it would introduce relative to typical measured NO_2 concentrations, 0.03 to 0.05 ppm, would be greater than 20 percent. The NO_2 impurity in the cylinder must be determined by an independent method which has no appreciable interference from NO. The triethanolamine- guaiacol-sulfite (TGS) manual method[10] is recommended. However, any other method which measures NO_2 directly and has no interference from NO may be used.

To determine the amount of NO_2 impurity in the NO cylinder, sample a diluted stream from the cylinder. The exact dilution will depend on the NO_2 concentration in the cylinder and the method chosen for analysis. Generally, dilutions of 1 to 100 or 1 to 50 will be adequate. Convert the NO_2 analyzed to ppm. Then calculate the NO_2 impurity using:

$$C_{NO_2} = \frac{(NO_2)_A \times F_T}{F_{NO}} \qquad \text{(A-3)}$$

where: C_{NO_2} conentration in cylinder, ppm

$(NO_2)_A$ = NO_2 concentration analyzed, ppm

F_T = Total flow at manifold, cm^3/min

F_{NO} = Flow from NO cylinder, cm^3/min

6.4.3 NO_2 Converter Efficiency. The efficiency of the NO_2 converter should be constant and linear over the range of operation. The NO_2 converter efficiency may be determined in the following manner. While the chemiluminescence analyzer is sampling clean air, adjust the zero controls for the NO and NO_x responses to read zero. Dilute the assayed cylinder of NO with clean air to produce approximately 0.9 ppm NO and adjust the span controls for the NO and NO_x responses to read exactly the NO concentration generated. The exact NO concentration is calculated as follows:

$$(NO) = \frac{F_{NO} \times C_{NO}}{F_T} \qquad (A\text{-}4)$$

where (NO) = NO concentration generated, ppm

C_{NO} = cylinder NO concentration, ppm

F_{NO} = NO flow, cm^3/min

F_T = total flow at manifold, cm^3/min

Note: If NO_2 impurity is present in the NO cylinder, adjust the span control for NO_x response to include the NO_2 impurity concentration assuming a converter efficiency of 1.

Observe and record the initial NO and NO_x readings. Next, add ozone to the NO stream to reduce the NO response to 0.8 ppm. Observe and record the final NO and NO_x readings. Repeat the above procedure adding ozone such that the NO response is decreased to 0.7, 0.6 and 0.5 ppm successively. Calculate the concentration of NO_2 generated by G.P.T. for each stepwise addition of ozone, the total NO_2 concentration generated, and the concentration of NO_2 converted to NO as follows:

$$NO_2 \text{ G.P.T., ppm} = NO_{\text{Initial, ppm}} - NO_{\text{Final, ppm}} \quad \text{(A-5)}$$

$$NO_2 \text{ Generated, ppm} = NO_2 \text{ G.P.T., ppm} + NO_2 \text{ Impurity, ppm}$$

$$NO_2 \text{ Converted, ppm} = NO_x \text{ Final, ppm} - NO_{\text{Final, ppm}}$$

Plot the NO_2 concentration converted (y-axis) versus the total NO_2 concentration generated (x-axis). The slope of this plot is the converter efficiency. A straight line indicates a constant converter efficiency over the 0 to 0.5 ppm range. If the converter efficiency is less than 0.90 (90 percent) or if it is not constant (i.e., nonlinear curve), the converter should be replaced or reactivated.

6.4.3.1 Frequency of Determination. The converter efficiency should be determined monthly when the instrument calibration is checked (Section 6.4.4.2).

6.4.4 NO_2 Calibration (0 to 0.5 ppm range).

6.4.4.1 Procedure. While sampling zero air from the gas phase titration apparatus, zero the NO, NO_x, and NO_2 detector reponses.

Adjust the NO flow rate to generate approximately 0.9 ppm NO by flow dilution (Section 6.4.3) and adjust the span controls to read the exact NO concentration generated. Any NO_2 impurity in the NO cylinder should be included (with an appropriate correction for dilution and converter efficiency) in the NO_x span adjustment.

Adjust the ozone source to add enough O_3 to decrease the NO response to approximately 0.45 ppm. This results in the generation of an equivalent amount of NO_2 which is used to span the NO_2 response. Allow the response of the instrument to stabilize and adjust the span control to give a direct readout of the generated NO_2, including any NO_2 impurity if present. Continue to decrease the O_3 concentration so as to produce NO_2 concentrations of approximately 0.30, 0.20, 0.10, and 0.05 ppm. Using this procedure the NO_2 generated can be determined by the following equation:

$$NO_{2\ Generated} = NO_{Initial} - NO_{Final} + NO_2\ Impurity,\ ppm \qquad (A\text{-}6)$$

where: $NO_{2\ Generated}$ = Total concentration of NO_2 generated, ppm

$NO_{Initial}$ = Initial concentration of NO, ppm

NO_{Final} = Concentration of NO after O_3 addition, ppm

Plot the total NO_2 concentration generated versus analyzer NO_2 response. A straight line should be obtained.

6.4.4.2 Frequency of Calibration. A complete calibration should be made once a month. Analyzers should be zeroed and spanned at

80 ± 5 percent of full scale daily, then adjusted for any drift that is detected. If the drift is more than ± 15 percent, the analyzer should be recalibrated.

7. Calculations

7.1 Determine the NO_2 concentration directly from the NO_2 calibration curve (Section 6.4.4.1).

7.2 Nitrogen dioxide concentrations in ppm can be converted to $\mu g/m^3$ at 25° C and 760 mmHg as follows:

$$(NO_2),\ \mu g/m^3 = (NO_2),\ ppm \times 1880 \times \frac{\mu g/m^3}{ppm} \qquad (A\text{-}7)$$

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A-1. Performance Specifications for Atmospheric-Chemiluminescence NO_2 Analyzers

Parameter	Unit[a]	Specification
Range[b]	ppm	multiple
Noise	ppm	0-0.005
Lower Detectable Limit	ppm	0.01
Zero Drift, 12-, 24-Hour	ppm	±0.02
Span Drift, 24-Hour	ppm	±0.02
Lag Time	minutes	0.5
Rise Time, 95 percent	minutes	1.0
Fall Time, 95 percent	minutes	1.0

[a]To convert from ppm to $\mu g/m^3$ at 25° C and 760 mm, multiply by 1880.

[b]No performance test required. All other performance specifications are tested on instrument operating in the 0-0.5 ppm range.

A-2.

Definitions of Performance Specifications

Range - Minimum and maximum concentrations which the system shall be capable of measuring.

Noise - Spontaneous, short duration deviations in the analyzer output about the mean output, which are not caused by input concentration changes.

Lower Detectable Limit - The minimum pollutant concentration which produces a signal of twice the noise level.

Zero Drift - The change in analyzer response to zero pollutant concentration over 12- and 24-hour periods of continuous unadjusted operation.

Span Drift - The change in analyzer response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation.

Lag Time - The time interval between a step change in input concentration at the analyzer inlet and the first observable corresponding change in the analyzer response that is equal to twice the noise in the instrument output.

Rise Time - The time interval between initial response and 95 percent of final response after a step increase in input concentration.

Fall Time - The time interval between initial response and 95 percent of final response after a step decrease in input concentration.

APPENDIX B. EQUATION FOR CALCULATION OF EFFECT OF EACH VARIABLE IN RUGGEDNESS TEST

1. $$A - a = \frac{s + t + u + v}{4} - \frac{w + x + y + z}{4}$$

2. $$B - b = \frac{s + t + w + x}{4} - \frac{u + v + y + z}{4}$$

3. $$C - c = \frac{s + u + w + y}{4} - \frac{t + v + x + z}{4}$$

4. $$D - d = \frac{s + t + y + z}{4} - \frac{u + v + w + x}{4}$$

5. $$E - e = \frac{s + u + x + z}{4} - \frac{t + v + w + y}{4}$$

6. $$F - f = \frac{s + v + w + z}{4} - \frac{t + u + x + y}{4}$$

7. $$G - g = \frac{s + v + x + y}{4} - \frac{t + u + w + z}{4}$$

APPENDIX C. RUGGEDNESS TEST DATA

Determination no.	NO_2 generated by gas phase titration, ppm	NO_2 analyzer response, ppm	Least squares slope	Observed result designation
1	0.082 0.192 0.309 0.419 0.537	0.085 0.192 0.304 0.420 0.540	0.9987	s
2	0.077 0.185 0.297 0.413 0.531	0.078 0.178 0.293 0.415 0.546	0.9770	t
3	0.082 0.192 0.314 0.432 0.547	0.080 0.193 0.302 0.425 0.545	1.009	u
4	0.084 0.197 0.315 0.438 0.551	0.085 0.190 0.305 0.420 0.541	1.028	v
5	0.080 0.190 0.303 0.426 0.540	0.084 0.195 0.304 0.422 0.550	0.9940	w
6	0.092 0.204 0.314 0.431 0.544	0.088 0.200 0.310 0.426 0.546	0.9977	x
7	0.077 0.182 0.292 0.417 0.532	0.078 0.176 0.288 0.400 0.555	1.023	y
8	0.093 0.206 0.320 0.443 0.559	0.090 0.199 0.315 0.436 0.558	1.003	z